STRUCTURE DETERMINATION OF *o*-CHLOROSTYRENE BUTADIENE COPOLYMER BY OZONOLYSIS

BY

RUPERT EDWIN LIGHT, JR.

B.S., Virginia Polytechnic Institute, 1941
M.S., University of Illinois, 1946

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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Introduction

The purpose of this investigation was to elucidate the structure of GR-S. Some of the more important factors affecting the qualities of synthetic rubber are, 1,2- versus 1,4-addition, the extent of cross-linking or branching, and the extent to which the different monomer units are bunched up rather than distributed along the polymer chain at random. A method capable of evaluating these factors would be invaluable in the study and control of synthetic rubber.

The most commonly used chemical method for studying the structure of diene polymers and copolymers involves oxidative scission of the double bonds in the polymer and separation and identification of the resulting fragments. Generally, the oxidizing agent will tend to carry these fragments past the aldehyde stage, so the most convenient method for obtaining a good yield of scission products is to operate under conditions such that carboxylic acids are produced.

Ozonolysis was employed in this investigation since it was the cleanest known method for the scission of double bonds. Adsorption chromatography and partition chromatography were used for the separation of the resulting complex mixtures of acids, since these methods were capable of giving a complete separation and a quantitative determination of the individual constituents in a single operation.

A copolymer of butadiene and *o*-chlorostyrene was selected in order to determine by means of chlorine analysis and ultraviolet absorption the quantity of phenyl groups in various fractions throughout the process. The ratio of the monomers was chosen so as to give a molar ratio the same as that of GR-S.

Discussion Of Results

The *o*-chlorostyrene was prepared by dehydration of *o*-

chlorophenylmethylcarbinol in the vapor phase by activated alumina. The 69.2/30.8 butadiene/*o*-chlorostyrene copolymer was prepared by emulsion polymerization in the Mutual recipe.[1]

The copolymer was ozonized and the ozonide was decomposed with dilute hydrogen peroxide.[2] The resulting acids were separated into water-soluble and water-insoluble acids. The excess hydrogen peroxide in the water-soluble fraction was decomposed with platinum oxide.

The non-volatile acids were obtained in 89 per cent yield by weight and 73 per cent yield by neutralization equivalent. On the basis of the oxygen content the water-insoluble acids were believed to contain some undecomposed ozonide or oxygen-containing functional groups other than carboxylic acids.

The water-soluble acids were separated by partition chromatography[3] and the water-insoluble acids were separated by both partition and adsorption chromatography using silicic acid as the adsorbing material.

The quantities of acids isolated and identified accounted for 32.4 per cent of the *o*-chlorostyrene units and 58.5 per cent of the butadiene units.

Succinic acid was obtained in a greater quantity and β-carboxyadipic acid in a much less quantity than expected, thereby indicating that the extent of 1,2-addition was less than the 20 per cent characteristic of GR-S.

The β-(*o*-chlorophenyl)-adipic acid was obtained in the quantity which indicates that the phenyl groups have entered the polymer chain in a random manner.

The results may also be interpreted on the assumption that side reactions are taking place on the 1,2-units to a greater extent than on the *o*-chlorostyrene or 1,4-butadiene units.

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VITA

The author was born in Patrick Springs, Virginia on June 22, 1918. He attended the public schools of St. Augustine, Florida, Critz, Virginia and Martinsville, Virginia, and was graduated from Martinsville High School in June, 1937. In the fall of that year, he entered Virginia Polytechnic Institute, receiving the degree of Bachelor of Science in Chemistry in June, 1941 and a commission in the U. S. Army. He served with the Ground Forces of the U. S. Army from July, 1941 to April, 1945. He was employed by the Hercules Powder Company as a chemist from March to August, 1945. In the fall of 1945 he enrolled in the Graduate College of the University of Illinois and received the degree of Master of Science in 1946. Since October, 1946 he has held a special research assistantship on the Rubber Research Program.

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